Multi-plateau magnetization curves of one-dimensional Heisenberg ferrimagnets

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Ground-state magnetization curves of ferrimagnetic Heisenberg chains of alternating spins S and s are numerically investigated. Calculating several cases of (S, s), we conclude that the spin-(S, s) chain generally exhibits $2s$ magnetization plateaux even at the most symmetric point. In the double- or more-plateau structure, the initial plateau is generated on a classical basis, whereas the higher ones are based on a quantum mechanism.

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I. INTRODUCTION

Ground-state magnetization curves of low-dimensional quantum spin systems have been attracting much recent interest due to their nontrivial appearance contrasting with classical behaviors. A few years ago there appeared an epochal argument [1] in the field. Generalizing the Lieb-Schultz-Mattis theorem [2,3], Oshikawa, Yamanaka, and Affleck proposed that magnetization plateaux of quantum spin chains should be quantized as

$$S_{\mathrm{unit}} - m = \mathrm{integer}\,, \tag{1.1}$$

where S_{unit} is the sum of spins over all sites in the unit period and m is the magnetization M divided by the number of the unit cells. Their argument caused renewed interest [4] in the pioneering calculations [5–7] of a bond-trimerized spin-$\frac{1}{2}$ chain and further stimulated extensive investigations into quantum magnetization process. Quantized magnetization plateaux were reasonably detected for spin-$\frac{1}{2}$ [8], spin-1 [9–11], and spin-$\frac{3}{2}$ [12,13] chains with modulated and/or anisotropic interactions. Totsuka [14], Cabra and Grynberg [15], and Honecker [16] developed calculations of general polymerized spin chains. Numerous authors have been making further theoretical explorations into extended systems including spin ladders [17–20] and layered magnets [21–23]. Experimental observations [24,25] have also followed.

Mixed-spin chains, which have vigorously been studied in recent years [26–36], also stimulate us in this context. Theoretical investigations into them are all the more interesting and important considering an accumulated chemical knowledge on ferrimagnetic materials. Kahn *et al.* [37] succeeded in synthesizing a series of bimetallic chain compounds such as $\mathrm{MM'(pba)(H_2O)_3{\cdot}2H_2O}$ (pba $=$ 1,3-propylenebis(oxamato) $=$ $\mathrm{C_7H_6N_2O_6}$) and $\mathrm{MM'(pbaOH)(H_2O)_3}$ (pbaOH $=$ 2-hydroxy-1,3-propylenebis(oxamato) $=$ $\mathrm{C_7H_6N_2O_7}$), where the alternating magnetic ions M and M$'$ are flexible variables and therefore the low-dimensional ferrimagnetic behavior could systematically be observed. Caneschi *et al.* [38] synthesized another series of mixed-spin chain compounds of general formula $\mathrm{M(hfac)_2NITR}$, where metal ion complexes $\mathrm{M(hfac)_2}$ with hfac $=$ hexafluoroacetylacetonate are bridged by nitronyl nitroxide radicals NITR. There also exist purely organic molecule-based ferrimagnets [39], where sufficiently small magnetic anisotropy, whether of exchange-coupling type or of single-ion type, is advantageous for observations of essential quantum mixed-spin phenomena.

Magnetization curves of Heisenberg ferrimagnetic chains were revealed by Kuramoto [33]. His argument covered an effect of next-nearest-neighbor interactions but the constituent spins were restricted to 1 and $\frac{1}{2}$. Although an alignment of alternating spins S and s ($S > s$) in a field, as described by the Hamiltonian

$$\mathcal{H} = \sum_{j=1}^{N} \Big[\ (1+\delta)(\boldsymbol{S}_j \cdot \boldsymbol{s}_j)_\alpha + (1-\delta)(\boldsymbol{s}_j \cdot \boldsymbol{S}_{j+1})_\alpha - H(S_j^z + s_j^z)\Big]\,, \tag{1.2}$$

with $(\boldsymbol{S} \cdot \boldsymbol{s})_\alpha = S^x s^x + S^y s^y + \alpha S^z s^z$, is so interesting as to possibly exhibit a series of quantized magnetization plateaux at $m = \frac{1}{2}(1), \frac{3}{2}(2), \cdots, S+s-1$, its magnetization curves have not systematically been studied so far. In spite of the vigorous argument, there are few reports on multi-plateau magnetization curves. It is true that a double-plateau structure lies in $\mathrm{NH_4CuCl_3}$ [21,25], but it is owing to the variety of exchange interactions. We here demonstrate that the ferrimagnetic chain (1.2) generally exhibits *a $2s$-plateau magnetization curve without any anisotropy and any bond polymerization*, namely, even at $\alpha = 1$ and $\delta = 0$. We believe that the present calculations will accelerate physical measurements on vast ferrimagnetic chain compounds lying unexploited in the field of both inorganic and organic chemistry.

The ground state of the isotropic Hamiltonian (1.2) without the Zeeman term, which is a multiplet of spin $(S-s)N$, exhibits elementary excitations of two distinct types [40]. The excitations of ferromagnetic aspect, reducing the ground-state magnetization, form a gapless dispersion relation, whereas those of antiferromagnetic

[46]. Considering that any magnetization plateau originates from an antiferromagnetic interaction, it is convincing that $2s$ of the total spin amplitude $S+s$ contributes to the plateaux appearing.

Let us turn back to Fig. 1 and observe the plateaux more carefully, especially as functions of α. In the cases of $s=\frac{1}{2}$, the plateaux are quite tough against the XY-like anisotropy. They are stable all over the antiferromagnetic-coupling region. These observations are in contrast with the classical behavior. The classical spin-(S,s) Heisenberg Hamiltonian also exhibits the magnetization plateau at $m=S-s$, but it survives only a small amount of XY-like anisotropy. For instance, the critical value for $(S,s)=(1,\frac{1}{2})$ is estimated as $\alpha_{\mathrm{c}}=0.943(1)$ [41]. The contrast between quantum spins and classical vectors suggests that the single plateaux in the quantum-spin magnetization curves may be attributed to the valence-bond excitation gap (*valence-bond gap*) rather than the Néel-state excitation gap (*Néel gap*). From this point of view, the α-dependences of the two coexistent plateaux in the cases of $s=1$ are interesting. The tiny second plateaux are much more stable against the XY-like anisotropy than the steady-looking initial steps. Since the Néel state reaches the saturation via a single-step excitation, the second and higher plateaux should originate from the valence-bond gap. The magnitude of the gap exponentially decreases with the increase of m, but the quantum gap-generation mechanism itself is rather tough against the XY-like anisotropy. The initial plateaux in the multi-step magnetization curves, which are relatively unstable against the XY-like anisotropy, may be attributed to the Néel gap. It seems that the lowest-lying magnetization plateaux are of quantum appearance for $s=\frac{1}{2}$ but are of classical aspect for $s\geq 1$.

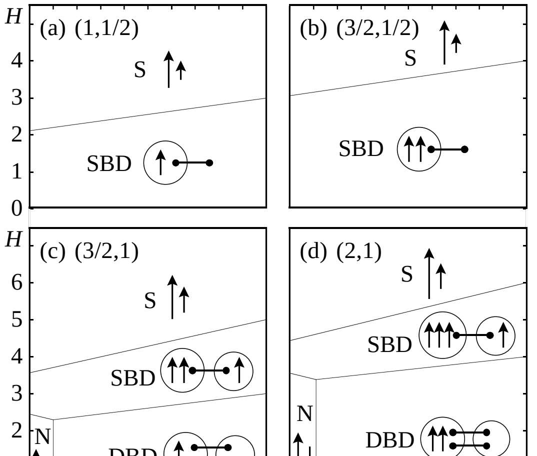

FIG. 3. The variational ground-state phase diagrams on the δH-plane for the Hamiltonian (2) with $\alpha=1$ at various values of (S,s).

In order to characterize the plateaux, we introduce a variational wave function for the ground state of the model (1.2) as

$$\begin{aligned}|\mathrm{g}\rangle &= c_{\mathrm{N}}\prod_{j=1}^{N}(A_j^\dagger)^{2S}(b_j^\dagger)^{2s}|0\rangle \\ &+\sum_{l=0}^{2s}c_{\mathrm{VB}}^{(l)}\prod_{j=1}^{N}(A_j^\dagger)^{2S-l}(a_j^\dagger)^{2s-l}(A_j^\dagger b_j^\dagger-B_j^\dagger a_j^\dagger)^{l}|0\rangle\,, \end{aligned} \tag{3.2}$$

where c_{N} and $c_{\mathrm{VB}}^{(l)}$ are the mixing coefficients. Since all the elemental states are asymptotically orthogonal to each other, the thermodynamic-limit variational ground states are considerably simple, as shown in Fig. 3, where we consider the Heisenberg point. The phase diagrams are exact on the line of $\delta=1$, where the spin-$(\frac{3}{2},1)$ chain, for example, reaches the saturation (S) via the double-bond dimer (DBD) and single-bond dimer (SBD) states. The point is that the $\delta=0$ ground states are better approximated by the decoupled-dimer states than by the Néel (N) states in the cases of $s=\frac{1}{2}$, while vice versa in all other cases. For $s=\frac{1}{2}$, the variational wave function (3.2) ends up with $c_{\mathrm{N}}=0$ all over the δ-H plain. The Néel-dimer crossover point δ_{c} is given by

$$\delta_{\mathrm{c}}=\frac{2Ss-A+B+C}{A-B+C}\,, \tag{3.3}$$

with

$$\begin{aligned} A &= \sum_{l=1}^{2s}\Bigg\{\frac{(2S-2s+l)!(2S-2s+l-1)!}{[(2S-2s)!]^2 l!(l-1)!} \\ &\quad\times[S(S+1)-(S-2s+l-1)(S-2s+l)] \\ &\quad\times[s(s+1)-(s-l)(s-l+1)]\Bigg\}^{1/2} \\ &\quad\Big/\sum_{l=0}^{2s}\frac{(2S-2s+l)!}{(2S-2s)!l!}\,, \\ B &= \sum_{l=0}^{2s}\frac{(2S-2s+l)!}{(2S-2s)!l!}(S-2s+l)(s-l) \\ &\quad\Big/\sum_{l=0}^{2s}\frac{(2S-2s+l)!}{(2S-2s)!l!}\,, \\ C &= \sum_{l=0}^{2s}\frac{(2S-2s+l)!}{(2S-2s)!l!}(S-2s+l) \\ &\quad\times\sum_{l=0}^{2s}\frac{(2S-2s+l)!}{(2S-2s)!l!}(s-l) \\ &\quad\Big/\sum_{l=0}^{2s}\frac{(2S-2s+l)!}{(2S-2s)!l!}\,. \end{aligned} \tag{3.4}$$

plateaux, with a quantum base, are stable over the whole antiferromagnetic-coupling region (a,b), while the initial plateaux in the multi-step process, taking on a classical character, less survive the XY-like anisotropy than the quantum higher plateaux (c,d). The existence of the second plateaux without any bond polymerization, which is the main issue in the present article, should be verified very carefully. So then we further employ an idea of the level spectroscopy [51], thus called, in analyzing the second plateau. Comparing the relevant excitation energies whose scaling dimensions are 2 at the critical point, we recognize the level crossing of them as the phase boundary. The thus-detected transitions are also plotted by broken lines in Fig. 6. The slight difference between the two estimates inevitably arises from the logarithmic corrections to the scaling law (3.5), where the level spectroscopy is more reliable than the naivest scaling analysis. Anyway, we may now fully be convinced of the existence of the novel multi-plateau magnetization curves.

IV. SUMMARY AND FUTURE ASPECT

The one-dimensional Heisenberg ferrimagnet with alternating spins S and s exhibits a $2s$-plateau magnetization curve even at the most symmetric point. It is interesting to compare the present spin-(S,s) ferrimagnetic chain with the spin-$\frac{1}{2}$ bond-polymerized chain of period $2(S+s)$, that is, the $(2S-1)$-times-ferromagnetic-antiferromagnetic-$(2s-1)$-times-ferromagnetic-antiferromagnetic chain. In the strong ferromagnetic-coupling limit, the latter may be regarded as equivalent to the former. In the same meaning, the spin-S antiferromagnetic Heisenberg chain can be viewed as a spin-$\frac{1}{2}$ bond-polymerized chain of period $2S$. Such replica chains generally exhibit magnetization plateaux in certain regions of the ratio of the ferromagnetic coupling J_{F} to the antiferromagnetic one J_{A}, $\gamma \equiv J_{\mathrm{F}}/J_{\mathrm{A}}$. However, in the case of the spin-$\frac{1}{2}$ ferromagnetic-ferromagnetic-antiferromagnetic chain which is the replica model of the spin-$\frac{3}{2}$ antiferromagnetic Heisenberg chain, Okamoto [6] and Hida [7] reported that the plateau vanishes at $\gamma = 4 \sim 5$ and therefore the pure Heisenberg chain exhibits no plateau. Thus the plateaux observed here in the most symmetric Heisenberg ferrimagnets still interest us to a great extent.

As we come up the steps, the plateau length exponentially decreases. It is hard to numerically observe the higher-lying plateaux, still harder experimentally. Only the first and second plateaux may lie within the limits of measurement. In this context, we are fortunate to have a series of bimetallic quasi-one-dimensional complexes $\mathrm{MM'(EDTA)\cdot 6H_2O}$ $(\mathrm{M}, \mathrm{M'} = \mathrm{Mn}, \mathrm{Co}, \mathrm{Ni}, \mathrm{Cu})$ [52]. Their exchange coupling constants are all about $10k_{\mathrm{B}}[\mathrm{K}]$ and thus the complete magnetization curves could technically be observed. Magnetization measurements on them, especially with $\mathrm{M} = \mathrm{Mn}\,(S=\frac{5}{2}), \mathrm{Co}\,(S=\frac{3}{2})$ and $\mathrm{M'} = \mathrm{Ni}\,(s=1)$, are encouraged. The plateaux would more or less be obscured in any actual measurement, but they, however small, should necessarily be detected by some anomaly in the magnetic susceptibility. The chemical modification of the bond alternation δ and/or the exchange anisotropy α must help us to directly observe the second-step plateaux, though we take main interest in the Heisenberg point.

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TABLE I. Estimates of the antiferromagnetic excitation gap from the ground state for the Hamiltonian (2) with $\alpha = 1$ and $\delta = 0$ by the use of the linear spin-wave theory (spin wave), the perturbation from the decoupled-dimer limit (perturbation), and the exact diagonalization (exact).

(S, s)	spin wave	perturbation	exact
$(1, \frac{1}{2})$	1	$\frac{11}{9}$	1.759(1)
$(\frac{3}{2}, \frac{1}{2})$	2	$\frac{17}{8}$	2.842(1)
$(\frac{3}{2}, 1)$	1	$\frac{16}{45}$	1.615(10)
$(2, 1)$	2	$\frac{11}{30}$	2.730(5)